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PLASTIC DEFORMATION OF HIGHLY DOPED SILICON

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Abstract

Heavily boron doped membranes are shown to be under tensile intrinsic stress with a negative intrinsic bending moment. However, the use of an oxide etch mask during membrane fabrication can alter the state of stress to an apparent compressive state with a positive bending moment. We propose that plastic deformation of the p^+ silicon beneath the compressively stressed oxide mask can account for this behavior.

Introduction

The intrinsic stress in heavily boron doped (p^+) silicon membranes is usually reported to be tensile [1-3]. However, an apparent state of compressive stress has also been observed [4]. In this paper, we show that the p^+ layer is under tensile stress, and that the appearance of the compressive behavior results from the use of an oxide etch mask. We suggest that plastic deformation of the p^+ silicon beneath the compressively stressed oxide can explain the observed behavior.

The introduction of electrically active impurities in single crystal silicon which form substitutional solid solutions with silicon atoms have been shown to substantially lower the activation energy for dislocation motion [5-9]. The neutral impurities, on the other hand, regardless of whether they are substitutional (germanium) or interstitial (oxygen), do not substantially affect dislocation mobility. The atomic size of the impurity is not an observable factor [8]. The decrease in the activation energy of the dislocation motion has been found to be stronger in donors [9]. The dislocation velocity change is observed when the impurity concentration exceeds the intrinsic carrier concentration [10].

The plastic deformation of crystalline solids occurs by the glide of dislocations, a time dependent process which depends upon the kinetics of dislocation motion in response to the

applied stress. Hence the critical shear stress for the onset of plastic deformation is the stress required to move dislocations.

In this work we suggest a mechanism for deformation of heavily boron doped silicon membranes under the strain field induced by a contacting layer when utilized as the etch mask in our sample fabrication. This layer can be chosen to be under either compressive stress and therefore induce an expansive strain (thermal oxide) or tensile stress and therefore induce a contractive strain (LPCVD nitride).

Experimental Results

P^+ membranes, of 2 mm x 2 mm to 10 mm x 10 mm in size, were fabricated by solid source diffusion of boron in 4 inch (100) silicon wafers [12,13]. The fabrication process is shown in Fig.1. The diffusion was done at 1125°C for 8 hours under 2% oxygen and 98% nitrogen gas flow resulting in a highly doped diffused layer of 6μ with concentrations above 8×10^{19}. The wafers were then cleaned following removal of the borosilicate glass (BSG) layer, formed during the diffusion, in buffered oxide etch. A number of the wafers were oxidized at 950°C for 12 hours in steam ambient resulting in 1.0 μ of thermal oxide, while others were deposited with LPCVD nitride at 800°C for 3 hours, resulting in 3000Å of nitride. The oxide, a compressively stressed material, and the nitride, a tensile stressed material, were used as etch masks for the anisotropic etchant (20% KOH). The membrane patterns were transferred to the back side of the wafers through the oxide using buffered oxide etch, and through the nitride using SF6 plasma. The wafers were etched from the backside in 20% KOH solution at 80°C following resist removal. Isopropanol was added towards the end to enhance the etch stop on the diffused layer.

At the completion of the etch, the membranes with the oxide mask buckled under the induced expansive shear strain of the thermal oxide, and the membranes with the nitride mask remained flat under the applied contractive shear strain of the LPCVD nitride. The oxide masked membranes, following the removal of the oxide, remained permanently deformed, maintaining the buckled shape of the removed oxide, while the nitride-masked membranes, upon removal of the nitride, remained permanently flat.

In a second series of experiments membranes of 4 mm x 4 mm to 25 mm x 25 mm in size were fabricated by solid source boron diffusion in 2 inch (100) silicon wafers at 1175°C for 3 hours in three groups [12]. The BSG layer, formed during diffusion, was used as an etch mask in group 1, a plasma enhanced CVD nitride deposited at 300°C was used as an etch mask in group 2, and a thermal oxide grown at 1100°C in a steam ambient was used as an

etch mask in group 3. The anisotropic etch, with 20% KOH, was done at 50°C for all wafers. The BSG layer etched through just as the p^+ membranes were complete, hence, the group 1 membranes experienced no load after the etch, and were flat. The intrinsic tensile stress in these membranes was estimated to be 30 MPa, measured using a standard bulge test [11]. These membranes exhibit a negative intrinsic bending moment. This is readily observed both from a slightly concave shape as fabricated, and from the fact that when the membrane is released from its support (by cutting), it curls upward (Fig.2). Membranes fabricated under the nitride etch mask remained flat prior and after removal of the nitride etch mask in all cases. The released membranes also curl upward indicating a negative intrinsic bending moment.

Membranes fabricated under thermal oxide etch mask deformed under the compressive stress of the thermal oxide after the completion of the anisotropic etch, and remained permanently deformed after removing the oxide mask in diluted HF (10:1). The complete removal of oxide was determined when a hydrophobic surface was observed. This result confirms the apparent compressive stress in p^+ membranes fabricated utilizing an oxide mask reported by Huff [4]. The intrinsic bending moment sign was opposite to the BSG and nitride-etch-mask fabricated membranes, as released portions of membranes curl downward (Fig.3). The apparent compressive behavior is due to a thin layer at the p^+ surface. This layer can be etched off in KOH. The deformed membranes gradually regained their flat (tensile) shape when immersed in 20% KOH solution at 80°C for a duration of 10 minutes (Fig. 4). The relative etch rate of the heavily boron doped material has not been successfully measured at this point, and it is therefore not clear how much of the p^+ material is removed from the front or the back side of the membrane. After the membranes regain their flat state in this process, a released portion of membranes curls downward, suggesting that the membrane still maintains a positive intrinsic bending moment.

Results and Discussion

The intrinsic tensile stress and negative bending moment in membranes fabricated under BSG etch mask are believed to be the true stress state of the heavily boron doped silicon. The state of stress has been related to the mismatch in the radii of boron and silicon [1,2,6]. The evidence from the membranes fabricated under both oxide and nitride masks suggests that the thermal oxide is responsible both for the buckled shape of the membranes after removal of the oxide, and for the reversal of the sign of the intrinsic bending moment.

We propose the following explanation. During the high temperature oxidation, high intrinsic compressive stress is developed in the oxide layer. A major part of the induced stress in thermal oxide grown on silicon is attributed to the thermal mismatch between the oxide ($\alpha_t = 0.35 \times 10^{-6} K^{-1}$) and Si ($\alpha_t = 4.5 \times 10^{-6} K^{-1}$) [14]. During the cool down of the oxidized wafer, the large stresses developed at the interface provide for a permanent local set in heavily doped silicon adjacent to the oxide - silicon interface. The oxide grown at 950°C results in approximately 8×10^8 dyn/cm^2 of stress in the oxide-silicon interface when cooled to 800°C, which is greater than plastic flow stress of silicon (3.5×10^8 dyn/cm^2) at this temperature [15]. Thermal oxides used in this study were grown at temperatures ranging from 950°C to 1100°C. Additional decrease of the activation energy of the dislocation motion induced by doping of electrically active boron impurities in silicon will further enhance the plastic flow. This argument is shown schematically in Fig.5. The released stress gradient due to the permanent set in a surface layer of the heavily doped silicon upon removal of the oxide layer will deform the membranes out of plane in a buckled mode shown in Fig.4. Removal of this layer in KOH returns the deformed membrane to its tensile stress dominated state.

An alternative explanation could be that during the oxidation, a complex boron-oxygen-silicon layer is formed near the surface of the heavily doped region which is compressively stressed, and unetchable in HF. Removal of this layer in KOH releases the induced compressive stress and the membranes regain their tensile shape. This explanation, however, would not necessarily explain the reversal of the sign of the intrinsic bending moment.

Concluding Remarks

The experimental evidence in this work show that heavily boron doped membranes are under tensile intrinsic stress and a negative intrinsic moment. Thermal oxidation can alter the state of intrinsic stress in heavily boron doped layer, possibly by plastic flow in the region adjacent to silicon-oxide interface.

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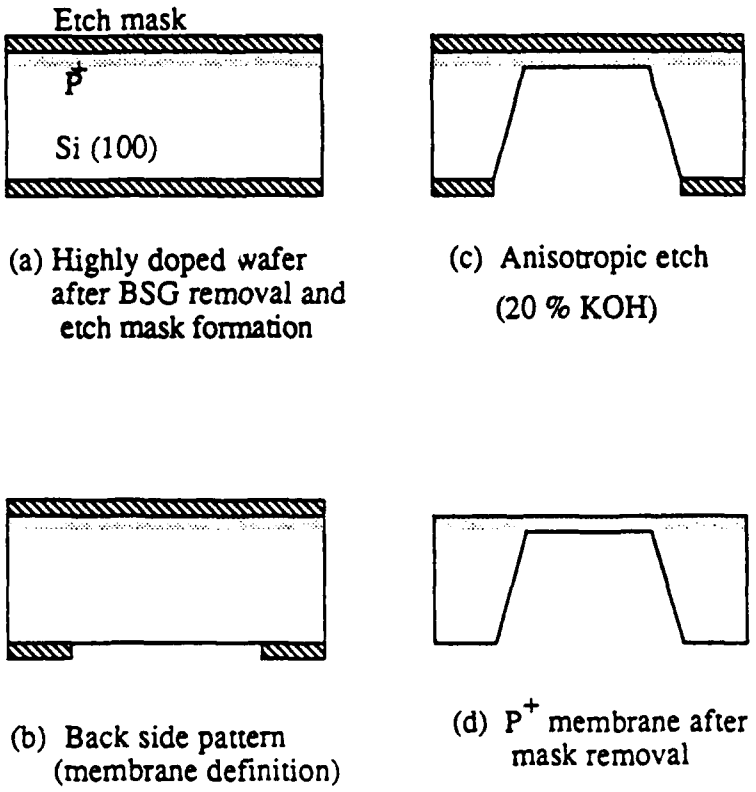


Fig. 1. Fabrication of heavily boron doped membrane

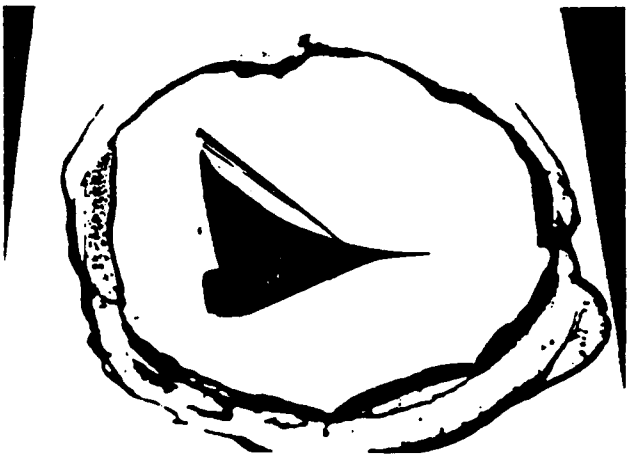
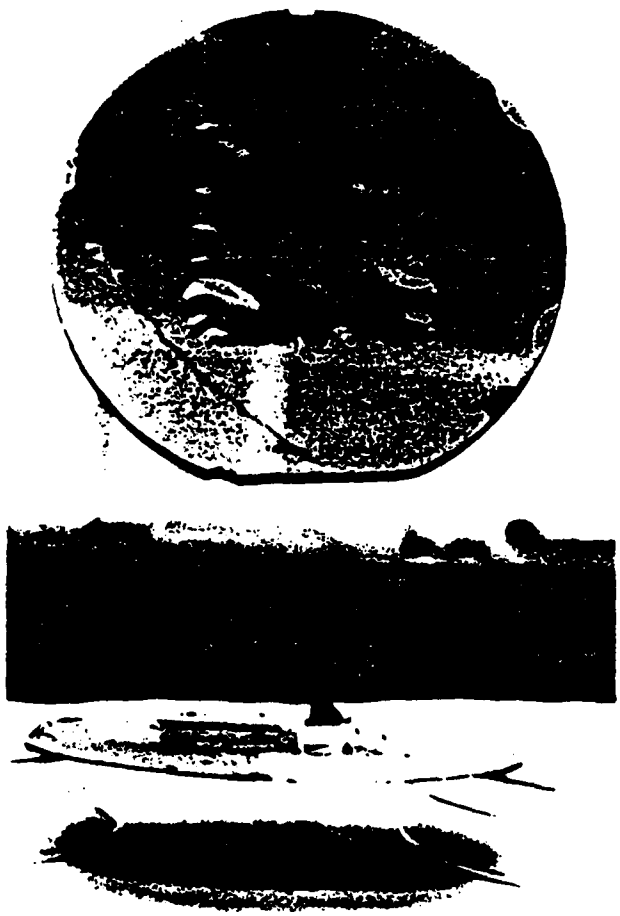


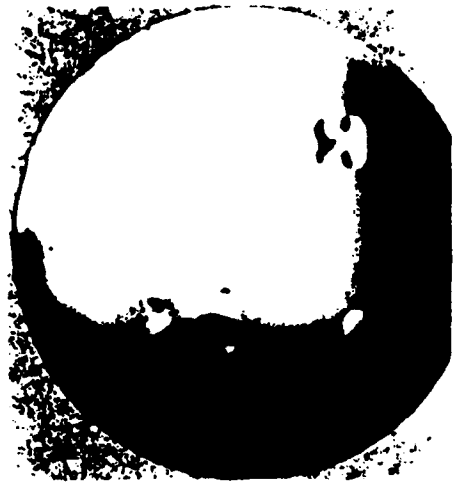
Fig. 2 . One inch square p+ membrane fabricated under BSG etch mask and mounted on a substrate: the released portion shows negative intrinsic bending moment



(a)

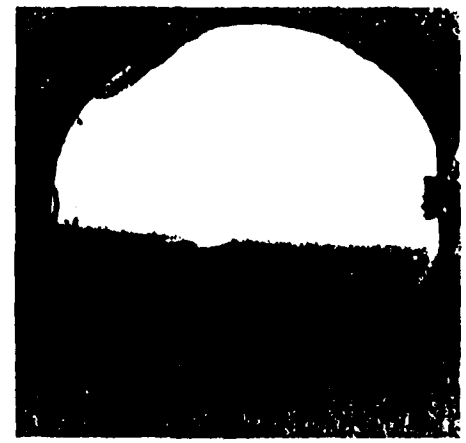
(b)

Fig. 3. Membrane fabricated under oxide etch mask.
(a) out of plane deformation when oxide is removed:
(b) the released portion shows positive intrinsic bending moment (view from back side)



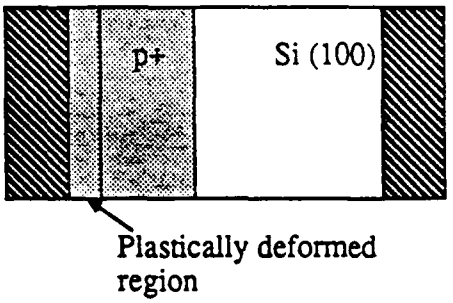
(a)

(b)

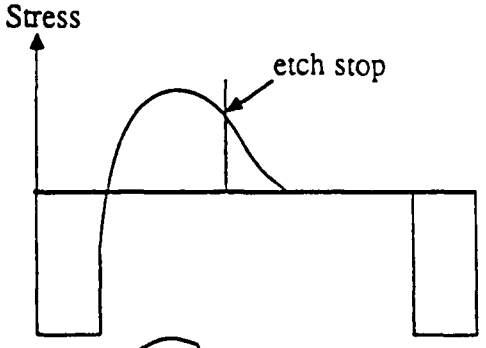


(c)

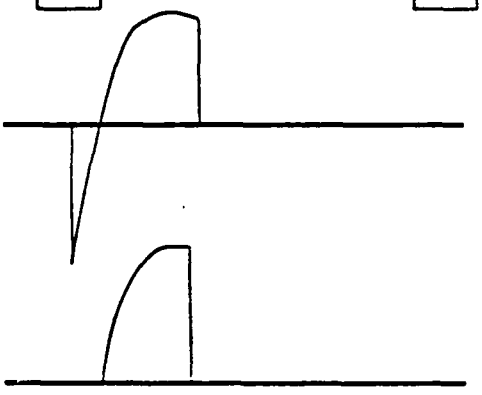
Fig. 4. Removal of deformation inducing layer; a) membranes deformed under remaining oxide etch mask; b) membranes remained deformed when oxide was removed; c) membranes flattened when immersed in KOH.



a) Boron doped Si with oxide etch mask

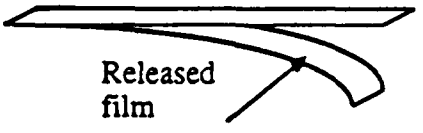


b) Stress redistribution from oxide to p+ region



c) Stresses when oxide is removed; compressive stress developed

d) Stress in p+ layer when deformation inducing layer removed (tensile dominated)



e) Released portion under a positive intrinsic bending moment

Fig. 5. Schematic stress transfer from oxide etch maskto p+ doped silicon (not to scale)